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Systematic Evaluation of 2,6-Linked Pyridine–Thiophene Oligomers

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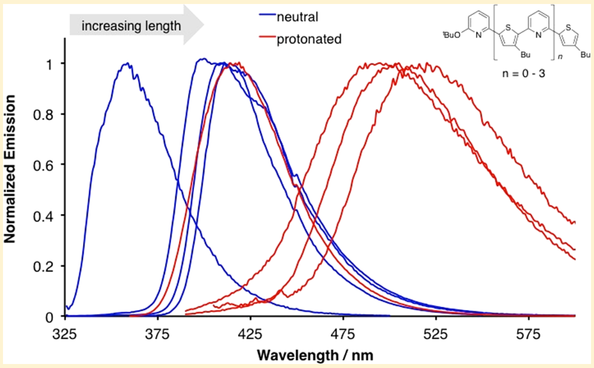
Ⓢ *Supporting Information*

ABSTRACT: An efficient synthesis of alternating 2,6-linked pyridine–thiophene (Py-Th) oligomers allows systematic evaluation of their optical and electrochemical properties. The six- and eight-ring oligomers are revealed to be brightly luminescent, even in the solid state. The oligomers are easily reduced but cannot be electrochemically oxidized. The longer oligomers have reduction potentials similar to those reported for pyridine–thiophene polymers of less defined structure. Protonation of the pyridine or substitution at C4 are shown to further modulate the electronic properties and, in combination with the low-lying absolute LUMO energies, these data suggest that the compounds are potential *n*-type materials worthy of further study.



INTRODUCTION

Thiophene-containing polymers are now ubiquitous in organic electronic materials, having found prominent application in, for example, organic solar cells and field effect transistors (FETs).[1] While such polymers benefit from stability and ease of preparation, the controlled synthesis of oligomeric species is an important complement: such oligomers are monodisperse and more readily purified, allowing better correlation of structure and properties.[2] Control of the band gap (HOMO–LUMO gap) of these materials remains challenging, and this has led to the development of donor–acceptor polymers and oligomers, the electronic properties of which are, ideally, controlled by the energies of the donor (D) fragment HOMO and acceptor (A) fragment LUMO.[3] There are now numerous thiophene-containing D–A oligomers and polymers, which in many cases do exhibit markedly reduced HOMO–LUMO gaps.

Our interests in thiophene D–A oligomer chemistry have their origins in our work on fluorescent 2,4,6-trisubstituted pyridines and the observation that, despite being the archetypal electron-deficient heterocycle, pyridine has been conspicuously understudied as a component in thiophene-based oligomeric materials.[4−6] We have previously reported the systematic, iterative synthesis of 2,5-linked pyridine–thiophene (Py-Th) oligomers,[7] and herein describe the preparation of the isomeric 2,6-linked Py-Th oligomers (Figure 1). We show that their optical and electrochemical properties make them a promising new class of materials, with absorption and emission that can be altered by protonation or substitution, solid state luminescence, and facile electrochemical reduction. While the maximum conjugation length is reached at the level of six- or eight-ring oligomers, the ability to vary the substituent at the pyridine C4 position allows modifications that induce behavior expected for much longer oligomers. Further exploration of these materials is thus both warranted and promising.

OLIGOMER SYNTHESIS

Beginning with 3-butylthiophene,[8] a pair of two-ring precursors were synthesized: **26a** was prepared by regioselective lithiation, transmetalation with zinc chloride, and Negishi coupling with 2-*tert*-butoxy-6-bromopyridine (Scheme 1).[9] Deprotection and sulfonylation then provided the corresponding triflate,[10] **26aTf**. Four- and six-ring oligomers (**26b–d**) were prepared by iterative homologation of **26a** with **26aTf** via lithiation/Negishi coupling, and the eight-ring oligomer was prepared by analogous coupling of a four-ring zincate and a four-ring triflate (Scheme 2).[11] **26TPT-H** and **26TPT-CN** were prepared by Negishi coupling of the 3-butylthiophenyl zincate with 2,6-dichloropyridine or 4-cyano-2,6-dichloropyridine.[12]

RESULTS AND DISCUSSION

Optical Properties. The optical properties of **26a–d** are remarkable in several respects (Figure 2 and Table 1). The two-ring compound (**26a**) has a relatively short absorption and emission wavelengths and low quantum yield. However, extension to four rings (**26b**) leads to a dramatic red shift in absorption and emission and a marked increase in emission efficiency. Extension to six rings (**26c**) continues these trends, and the extinction coefficient now becomes appreciable, reaching almost 50000 M^{-1} cm^{-1}. In addition, the emission of **26c** is now visible. The eight-ring compound **26d** has an emission maximum slightly further into the visible region, an extinction coefficient (6.0×10^5 M^{-1} cm^{-1}) about half that of fluorescein, and a very high quantum efficiency ($\phi = 0.74$).

In addition to bright luminescence in solution, oligomers **26c,d** exhibit solid-state emission, readily visible in ambient light. They are substantially more emissive ($\phi = 0.09$) as amorphous

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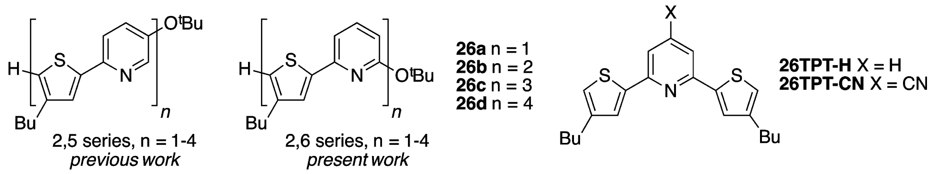
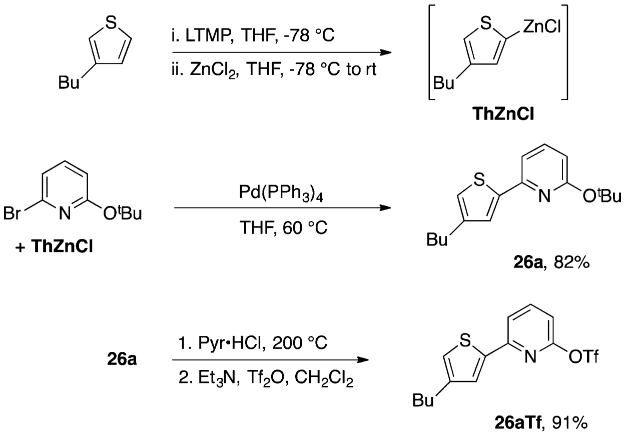


Figure 1. 2,6-Linked pyridine−thiophene (Py-Th) oligomers.

Scheme 1. Synthesis of Building Blocks 26a and 26aTf[a]



[a] See Experimental Section for details.

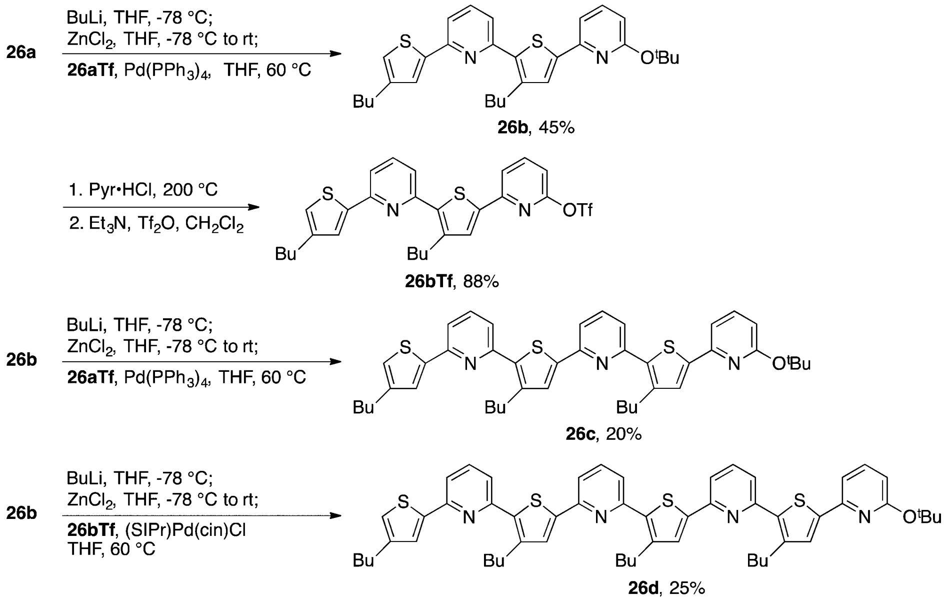
thin films than typical poly- and oligothiophenes lacking pyridine rings (e.g., poly(3-octylthiophene), $\phi = 0.04$)[1b] or most known pyridine−thiophene conjugates with a higher proportion of thiophene rings.[6] The excitation and emission maxima are red-shifted by 40−50 nm in the solid state, consistent with increased planarization due to packing forces.

Protonation of **26a−d** induces red shifts of 40−60 nm in absorption and as much as 100 nm in emission; **26c,d** now have both absorption and emission entirely in the visible region, although the quantum yields are appreciably diminished (~0.10). Protonation of the pyridine thus serves as a simple method for modulating the optical properties of **26a−d** and suggests that irreversibly functionalized analogues such as *N*-oxides and *N*-alkylated species are worth preparing.

During the course of this work, a series of compounds similar to **26a−c** was reported,[6h] which had (ethylenedioxy)thiophenes in place of 3-butylthiophene units and a terminal −H instead of −O^{t}Bu but which possessed the 2,6-linkage on the pyridine ring; the maximum oligomer length was six rings. The absorption and emission maxima of the four- and six-ring compounds come at longer wavelength (by 20−40 nm) than those of **26b,c**. The extinction coefficients and quantum yields were also high, although somewhat lower than those reported here: e.g., λ_{max}(abs) 390 nm; λ_{max}(em) 485 nm, $\varepsilon = 31000\ M^{-1}\ cm^{-1}$, and $\phi = 0.41$ for the compound analogous to **26c**. In that study, which included X-ray crystallographic characterization, it was proposed that the oligomers possessed a well-defined "coiled" structure in solution and that this conformational preference lent rigidity to the excited state, leading to the unusually high quantum yields. As **26a−d** are amorphous solids, we are unable to make a comparable analysis. However, X-ray crystallographic analysis of **26TPT-CN** reveals all three rings to be coplanar (see the Supporting Information)

The overall similarities between **26c** and **26d** indicate that the optical properties of these oligomers converge very quickly, and the six- and eight-ring compounds represent the conjugation limit for this system. The short λ absorption features observed for **26d** but not **26c** are similar to the absorbances of **26a**. This suggests that **26d** does not actually behave as an eight-ring

Scheme 2. Synthesis of 26a−d[a]



[a] (SIPr)Pd(cin)Cl = (1,3-bis(2,6-diisopropylphenyl)-4,5-dihydroimidazol-2-ylidenyl)palladium cinnamyl chloride. See the Experimental Section.

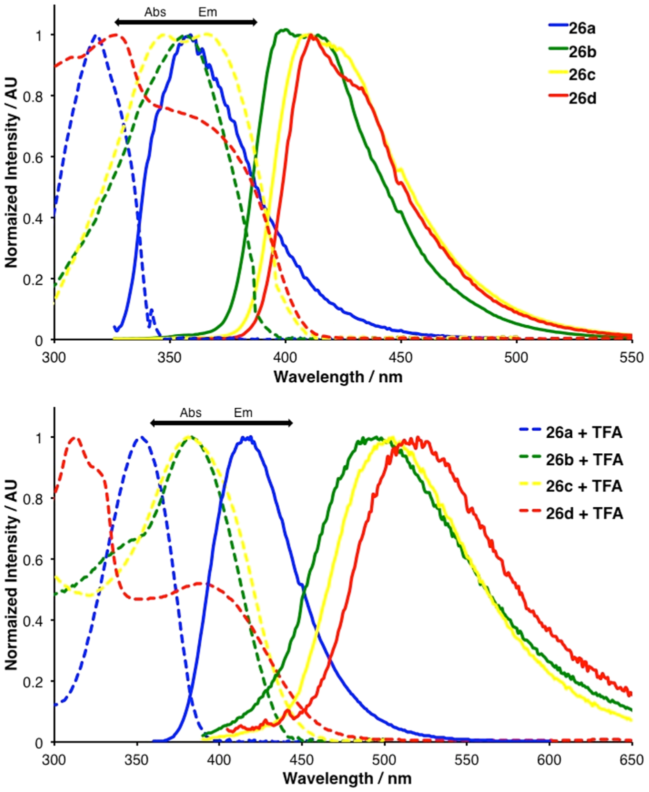


Figure 2. (top) Normalized absorbance (dashed) and emission (solid) of **26a**−**d** (CH_3CN). (bottom) Normalized absorbance and intensity in the presence of excess TFA (CH_3CN).

Table 1. Optical Properties of 26a−d

	$\varepsilon/10^4$ M^{-1} cm^{-1} ^{a,b}	λ_{max}(abs)/nm −/+ TFA^{a,c}	λ_{max}(em)/nm −/+ TFA^{a,c}	$\phi^{c,d}$
26a		320/351	360/415	0.05
26b		355/382	410/494	0.60
26c	4.7	368/386	415/503	0.69
film^e		*395/−*	*465/−*	*0.09*
26d	6.0	370/395	422/520	0.74
film^e		*395/−*	*475/−*	*0.09*

^{a}Values for longest wavelength λ_{max}. ^{b}In $CHCl_3$. ^{c}In CH_3CN. ^{d}Quantum yields for neutral species relative to PPO (ϕ = 0.94 in cyclohexane) for **26a** and DPA (ϕ = 1, in cyclohexane) for **26b**−**d**. PPO = 2,5-diphenyloxazole and DPA = 9,10-diphenylanthracene. ^{e}Thin film spin-coated from benzene.

system but rather as a six-ring system + a two-ring system or, in the presence of TFA, a six-ring system + two one-ring systems (Figure 2). This saturation with the meta-linked architecture contrasts with observations from the para-isomeric 2,5-linked pyridine−thiophene oligomers, which have not yet reached maximum conjugation length at eight rings.

Electrochemical Properties. The electrochemical properties of **26a**−**d** are also noteworthy (Figure 3 and Table 2) and reveal a strongly electron-accepting character that suggests them as *n*-type materials. A single, reversible reduction wave at E_{onset} = −2.75 V vs Fc/Fc$^+$ is observed for **26a**. However, the four-ring compound (**26b**) undergoes three well-defined reductions, the first of which comes at −2.42 V; **26c**,**d** each show four and five discernible redox events, respectively, at progressively less negative onset voltages (−2.31 and −2.20 V).[13] While the reductions of **26c**,**d** are comparable to those of the most easily reduced analogous polymers,[5d] we are unable to oxidize these oligomers electrochemically. Their properties are thus the opposite of typical thiophene oligomers—and many pyridine−thiophene oligomers with a higher proportion of thiophene rings—which undergo facile oxidation but not reduction. We suspect that the imperfect reversibility observed in the cyclic voltammograms of **26c**,**d** reflects loss of *tert*-butyl radical from multiply reduced species. It is anticipated that removal of the terminal alkoxy group will resolve this issue.

The capacity of the six- and eight-ring compounds to accept multiple electrons parallels the behavior of the related 2,5-series, although the reduction potentials are more negative for **26a**−**d**. The combination of E_{onset} and the optical band gap, E_g, derived from the absorption onset allow the estimation of absolute HOMO and LUMO energies for these oligomers (Table 2).[14] Assuming that the value of −4.46 eV is equivalent to 0.0 V vs the normal hydrogen electrode (NHE), and taking into consideration that the Fc/Fc$^+$ redox couple potential has a value of 0.53 V vs SCE (standard calomel electrode) in THF, we can approximate the formal potential of Fc/Fc$^+$ to be −5.23 eV in THF, since the difference between SCE and NHE has a value of 0.24 V. Therefore, the absolute LUMO energy can be written as $E_{LUMO} = -(E_{red} + 5.23\ \text{eV})$. Treating the HOMO−LUMO gap as being equal to the energy of the absorption onset then provides an estimate of the absolute HOMO energy.

To the extent that the LUMO energies of **26c**,**d** are predictive, we note that they lie close to that of pentafluorophenyl-terminated tetrathiophene (E_{LUMO} = −2.85 eV),[15] a representative *n*-type material. The HOMO levels, in a departure from the expectations of D−A oligomer design, remain almost constant across **26a**−**d**, with the variation in the HOMO−LUMO gap coming primarily from lowering of the LUMO energies.

Impact of C4 Substitution. The meta substitution pattern apparently limits the maximum conjugation length of these oligomers.[16] As briefly noted, structural analysis of a related system suggested a coiled structure for the four- and six-ring oligomers;[6h] if the same is true for **26b**−**d**, this could be the origin of the limit on conjugation length. This observation aside, meta substitution provides an important advantage in allowing for the addition of a third substituent without impacting the degree of conjugation of the molecules. This is illustrated by the changes in optical properties upon introduction of a cyano group at C4 (**26TPT-H** vs **26TPT-CN**; Figure 4). The 2,6-dithienylpyridine **26TPT-H** has excitation and emission maxima (334/377 nm) intermediate between those of the two- and four-ring compounds **26a**,**b**. In contrast, the corresponding 4-cyano derivative, **26TPT-CN**, has excitation and emission maxima very similar to those of the six-ring compound **26c**, despite itself possessing only three rings (Table 3). This effect is also seen in the protonated forms of the molecules, with **26TPT-CN**·H$^+$ having optical properties directly comparable to those of **26c**·H$^+$. The absorptivity and emissivity of **26TPT-CN** are noticeably lower than those of **26c**. These presumably reflect the influence of conjugation length on the magnitude of the transition dipole for the $S_0 \rightarrow S_1$ transition, which necessarily influences the efficiency of $S_1 \rightarrow S_0$ emission as well.[16]

■ CONCLUSION

This concise, systematic study of 2,6-linked pyridine−thiophene oligomers has revealed them to have unanticipated optical and electronic properties that make them potentially useful species for materials applications. The oligomers can be readily assembled by iterative coupling of two- and four-ring precursors.

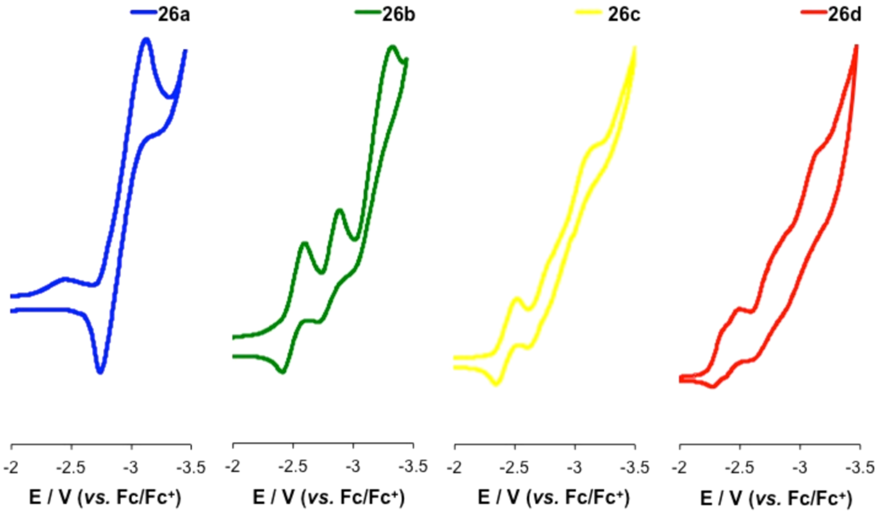


Figure 3. Reductive portion of the cyclic voltammograms. Conditions: 1 mM in THF, 0.1 M Bu_4NClO_4, scan rate 50 mV s^{-1}, glassy-carbon working electrode, Pt-wire counter electrode, Ag/AgCl reference electrode, ferrocene (Fc) internal reference.

Table 2. Absolute HOMO and LUMO Energies for 26a–d[a]

	E_{red}, V	E_g, V	HOMO, eV	LUMO, eV
26a	−2.75	3.56	−6.04	−2.48
26b	−2.42	3.11	−5.92	−2.81
26c	−2.31	3.02	−5.94	−2.92
26d	−2.20	2.99	−6.02	−3.03

[a] E_{red} = onset reduction potential; E_g = optical band gap from absorption onset. See ref 16.

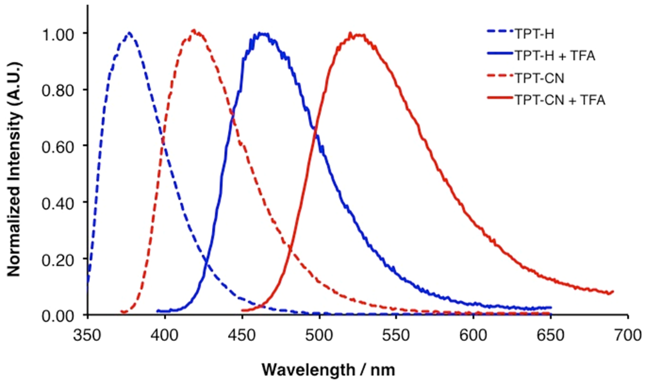


Figure 4. Normalized absorption (dashed) and emission (solid) spectra for **26TPT-H** and **26TPT-CN** without and with excess TFA.

Table 3. Optical Properties of 26TPT-H and 26TPT-CN

	$\varepsilon/10^4$ M^{-1} cm^{-1} [a,b]	λ_{max}(abs)/nm −/+ TFA[a,c]	λ_{max}(em)/nm −/+ TFA[a,c]	ϕ[c,d]
26TPT-H	1.6	334/390	377/464	0.54
26TPT-CN	2.0	355/382	410/494	0.10
26c	4.7	368/386	415/503	0.69 (0.09)[d]

[a] Values for longest wavelength λ_{max}. [b] In $CHCl_3$. [c] In CH_3CN. [d] Quantum yields for neutral species relative to PPO (ϕ = 0.94 in cyclohexane) for **26TPT-H** and DPA (ϕ = 1, in cyclohexane) for **26TPT-CN** and **26c**. PPO = 2,5-diphenyloxazole and DPA = 9,10-diphenylanthracene. [e] Thin film quantum yield of **26c** in parentheses: thin film spin-coated from benzene.

They prove to be surprisingly emissive, even in the solid state, and exhibit the capacity for multielectron reduction. These features are in distinct contrast to those of polythiophenes or pyridine–thiophene oligomers containing a higher proportion of thiophene rings.[6] The absolute LUMO energies are low-lying for such simple oligomers. In conjunction with the powerful influence of an electron-withdrawing group at C4 of the pyridine, these make the pyridine–thiophene conjugates promising candidates for *n*-type materials. Ongoing efforts include the preparation of longer CN-substituted oligomers, compounds lacking the terminal oxygen functionality and *N*-functionalized species,[17] as well as the evaluation of the solid-state electronic properties of the oligomers.

■ EXPERIMENTAL SECTION

General Considerations. Synthetic procedures were carried out under an inert atmosphere, in dry solvent, using standard Schlenk techniques, unless otherwise noted. All reagents and solvents were reagent grade and were used without further purification unless otherwise specified. Flash chromatographic purification was performed using silica gel Merck 60 (particle size 0.040–0.063 mm) or deactivated (5% water by weight) neutral aluminum oxide Sigma-Aldrich, Brockmann I, packed in glass columns; the eluting solvent for each purification was determined by thin-layer chromatography (TLC). Analytical thin-layer chromatography was performed using Merck TLC silica gel 60 F254 or Macherey–Nagel POLYGRAM ALOX N/UV254.

^1H NMR chemical shifts are reported in parts per million (ppm) relative to the solvent residual peak ($CDCl_3$, 7.26 ppm). Multiplicities are given as s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), and m (multiplet), and the coupling constants, *J*, are given in Hz. ^{13}C NMR chemical shifts are reported relative to the solvent residual peak ($CDCl_3$, 77.0 ppm).

IR frequencies are given in cm^{-1}. HRMS data were acquired on a QTOF instrument with an ESI source. All solid synthetic products were noncrystalline (oils or sticky solids), precluding melting point determination.

Cyclic voltammetry conditions: 1 mM compound, 0.1 M Bu_4NClO_4 as supporting electrolyte in THF, scan rate 100 mV s^{-1}, glassy-carbon working electrode (ϕ = 0.3 cm), Pt-wire counter electrode, Ag/AgCl reference electrode, added ferrocene (Fc) as internal reference.

Fluorescence measurements were carried out in spectroscopic grade CH_3CN using 450 W xenon lamp excitation with 1 nm excitation and 1 nm emission slit widths. Emission spectra were obtained by exciting at the longest wavelength absorption maxima. Quantum yields were determined by standard methods,[18] using 2,5-diphenyloxazole (PPO; ϕ = 0.94, in cyclohexane) or 9,10-diphenylanthracene (DPA; ϕ = 1, in cyclohexane) as the standards.[19] The samples were diluted to optical transparency ($A \leq 0.05$), and the integrated emission intensity was compared to an iso-absorptive solution of the standards in degassed solvent.

For extinction coefficient determination, four independent solutions of different concentration were prepared, with absorption between 0.04 and 0.10 au. The value of ε was calculated by linear least-squares fitting of plots of A vs concentration. All fits gave R^2 values of ≥0.98.

General Negishi Procedure. Flame-dried flasks were used, and all solutions were handled under nitrogen. In a Schlenk flame-dried flask, a THF solution (0.1−0.5 M) of component A was cooled to −78 °C and treated with base (BuLi or LiTMP). After 40 min of stirring at −78 °C, a THF solution of $ZnCl_2$ (0.2−0.7M) was slowly added, the cooling bath was removed, and the reaction mixture was warmed to room temperature and stirred for 40 min. This mixture was then transferred via cannula to a two-neck flask equipped with a condenser and containing a THF solution of component B (0.3−0.5M) and the palladium catalyst. This final reaction mixture was heated to 60 °C and stirred overnight. After the mixture was cooled to room temperature, a few drops of water were added and the solvent was removed in a rotary evaporator. The mixture was dissolved in dichloromethane and washed with an EDTA saturated solution, which was washed three times with dichloromethane. The combined organic fractions were washed with brine, dried over Na_2SO_4, and concentrated. The crude product was purified by column chromatography.

6-Bromo-2-(1,1-dimethylethoxy)pyridine. To a solution of 2,6-dibromopyridine (21.1 mmol, 5.00 g) in 75 mL of toluene was added potassium *tert*-butoxide (23.2 mmol, 2.60 g), and the reaction mixture was refluxed overnight. After it was cooled to room temperature, the crude mixture was filtered through Celite and the solvent was removed in vacuo. Purification by column chromatography (silica, ethyl acetate/hexanes 1/9) afforded the product as a colorless liquid (15.1 mmol, 71% yield). NMR data were consistent with those previously reported.[20]

^{1}H NMR (400 MHz, $CDCl_3$, 300 K, δ): 7.34 (t, J = 7.8, 1H), 6.97 (d, J = 7.5, 1H), 6.57 (d, J = 8.1, 1H), 1.58 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, 300 K, δ): 163.0, 140.0, 137.6, 119., 111.4, 80.9, 28.4.

*Compound **26a**.* This compound was prepared by the general Negishi cross-coupling procedure: component A, 3-butylthiophene (12.00 mmol, 1.68 g); base, LiTMP (12.2 mmol); $ZnCl_2$ (13.5 mmol, 1.84 g); catalyst, $Pd(PPh_3)_4$ (0.4 mmol, 462 mg); component B, 2-*tert*-butoxy-6-bromopyridine (34.33 mmol, 7.90 g). It was purified by column chromatography (silica, CH_2Cl_2/hexanes 1/9, 2/8) to afford a light yellow liquid (2.41 g, 76%).

R_f(silica, EtOAc/hexanes 1/9) = 0.57. ^{1}H NMR (400 MHz, $CDCl_3$, 300 K, δ): 7.49 (dd, J = 8.1, 7.4, 1H), 7.35 (dd, J = 1.3, 1H), 7.14 (dd, J = 7.4, 0.6, 1H), 6.93 (d, J = 1.3, 1H), 2.61 (t, J = 7.6, 2H), 1.65 (s, 9H), 1.61 (m, 2H), 1.38 (sextet, J = 7.4, 2H), 0.94 (t, J = 7.4, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 300 K, δ): 163.5, 149.5, 145.3, 144.1, 138., 125.0, 121.7, 110.9, 110.1, 79.7, 32.6, 30.3, 28.6, 22.3, 13.9. HR-MS (ESI, $C_{17}H_{23}NNaOS$, $[M + Na]^+$): calculated, 312.1398; found, 312.1394.

*Compound **26aOH**.* Pyridine hydrochloride (112 mmol, 13 g) was added to **26a** (4.5 mmol, 1.3 g), and the neat mixture was heated to 200 °C for 4 h. The mixture was then dissolved in water, neutralized with 1 M NaOH solution, and extracted three times with CH_2Cl_2. The combined fractions were combined, dried over Na_2SO_4, and concentrated in vacuo. The crude mixture was passed through a plug of alumina (deactivated alumina, CH_2Cl_2) to afford the product (1.01 g, 96%), which was used immediately in the next reaction.

^{1}H NMR (400 MHz, $CDCl_3$, 300 K, δ): 10.76 (bs, 1H), 7.52 (d, J = 1.6, 1H), 7.40 (dd, J = 9.2, 7.2, 1H), 6.99 (dd, J = 2.2, 1.1, 1H), 6.45 (m, 2H), 2.63 (t, J = 7.48, 2H), 1.63 (m, 2H), 1.38 (m, 2H), 0.95 (t, J = 0.95, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 300 K, δ): 164.8, 144.9, 141.4, 141.1, 135.5, 128.3, 122.3, 118.2, 103.7, 32.4, 30.2, 22.3, 13.9. HR-MS (ESI, $C_{13}H_{15}NNaOS$, $[M + Na]^+$): calculated, 256.0772; found, 256.0769.

*Compound **26aTf**.* A solution of **26aOH** (4.32 mmol, 1.01 g) in 15 mL of CH_2Cl_2 was treated with triethylamine (4.75 mmol, 0.65 mL). The reaction mixture was cooled to 0 °C, trifluoromethanesulfonic anhydride (4.75 mmol, 0.80 mL) was slowly added, and the cooling bath was removed. The reaction mixture was stirred for 4 h at room temperature, at which point it was quenched with water. The water phase was neutralized with $NaHCO_3$ saturated solution and extracted three times with CH_2Cl_2. The combined organic fractions were dried over Na_2SO_4, and the solvent was removed in vacuo. The crude mixture was passed through a plug of alumina (deactivated alumina, CH_2Cl_2/hexanes 1/1) to afford the product (1.42 g, 90%).

^{1}H NMR (400 MHz, $CDCl_3$, 300 K, δ): 7.83 (t, J = 7.8, 1H), 7.61 (dd, J = 7.8, 0.6, 1H), 7.51 (d, J = 1.4, 1H), 7.05 (d, J = 1.4, 1H), 6.97 (dd, J = 7.8, 0.6, 1H), 2.63 (t, J = 7.6, 2H), 1.62 (m, 2H), 1.38 (m, 2H), 0.94 (t, J = 7.3, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 300 K, δ): 155.4, 152.6, 144.6, 141.4, 141.3, 127.9, 124.1, 118.5, 118.3 (q, J_{C-F} = 318, 1C), 112.2, 32., 30.2, 22.3, 13.9. HR-MS (ESI, $C_{14}H_{14}F_3NNaO_3S_2$, $[M + Na]^+$): calculated, 388.0259; found, 388.0259.

*Compound **26b**.* This compound was prepared by the general Negishi cross-coupling procedure: component A, **26a** (2.50 mmol, 0.723 g); base, BuLi (2.55 mmol); $ZnCl_2$ (3.25 mmol, 0.440 g); catalyst, $Pd(PPh_3)_4$ (0.150 mmol, 0.173 g); component B, **26aTf** (2.60 mmol, 0.950 g). It was purified by column chromatography (deactivated alumina, CH_2Cl_2/hexanes 1/9, 1/4, 3/7, 2/3) to afford a yellow solid (0.78 g, 62%).

^{1}H NMR (400 MHz, $CDCl_3$, 300 K, δ): 7.67 (t, J = 7.8, 1H), 7.53−7.42 (m, 4H), 7.41 (s, 1H), 7.21 (dd, J = 7.5, 0.6, 1H), 7.00 (d, J = 1.3, 1H), 6.51 (dd, J = 8.2, 0.6, 1H), 3.09 (t, J = 7.8, 2H), 2.65 (t, J = 7.7, 2H), 1.77−1.62 (m, 4H), 1.68 (s, 9H), 1.50−1.35 (m, 4H), 0.96 (t, J = 7.3, 3H), 0.95 (t, J = 7.3, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 300 K, δ): 163.2, 153.3, 152.1, 149.4, 144.7, 144.4, 144.1, 143.0, 138.7, 138.1, 137.0, 127.7, 126.1, 122.6, 119.7, 116.0, 111.3, 110.3, 79.8, 32.8, 32.6, 30., 29., 28.7, 22.8, 22.4, 14.1, 13.9. HR-MS (ESI, $C_{30}H_{37}N_2OS_2$, $[M + H]^+$): calculated, 505.2341; found, 505.2343.

*Compound **26bOH**.* Pyridine hydrochloride (18 mmol, 2.1 g) was added to **25a** (0.36 mmol, 0.181 g), and the neat mixture was heated to 190 °C for 4 h. The mixture was then dissolved in water, neutralized with 1 M NaOH solution, and extracted three times with CH_2Cl_2. The combined fractions with dried over Na_2SO_4 and concentrated in vacuo. The crude mixture was passed through a plug of alumina (deactivated alumina, CH_2Cl_2) to afford the product (155 mg, 93%).

^{1}H NMR (500 MHz, $CDCl_3$, 300 K, δ): 13.25 (bs, 1H), 7.71 (t, J = 8.0, 2.6, 1H), 7.65 (s, 1H), 7.54−7.49 (m, 3H), 7.39 (d, J = 7.8, 1H), 7.02 (s, 1H), 6.67 (d, J = 7.1, 1H), 6.56 (d, J = 8.0, 1H), 3.02 (t, J = 8.0, 2H), 2.65 (t, J = 7.6, 2H), 1.60−1.74 (m, 2H), 1.68−1.62 (m, 2H), 1.50−1.45 (m, 2H), 1.42−1.38 (m, 2H), 0.99−0.94 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, 300 K, δ): 163.9, 152.5, 151.9, 144.3, 144.1, 142.8, 142.1, 140.8, 140.5, 137.3, 134.4, 130.4, 126.3, 122.9, 119.4, 117.8, 116.8, 105.1, 32.6, 32.3, 30.3, 29.8, 22.7, 22.3, 14.0, 13.9. HR-MS (ESI, $C_{26}H_{29}N_2OS_2$, $[M + H]^+$): calculated, 449.1721; found, 449.1712.

*Compound **26bTf**.* A solution of **26bOH** (0.37 mmol, 0.167 g) in 5 mL of CH_2Cl_2 was treated with triethylamine (0.59 mmol, 0.09 mL). The reaction mixture was cooled to 0 °C, trifluoromethanesulfonic anhydride (0.55 mmol, 0.09 mL) was slowly added, and the cooling bath was removed. The reaction mixture was stirred for 4 h at room temperature, at which point it was quenched with water. The water phase was neutralized with $NaHCO_3$ saturated solution and extracted three times with CH_2Cl_2. The combined organic fractions were dried over Na_2SO_4, and the solvent was removed in vacuo. The crude mixture was passed through a plug of alumina (deactivated alumina, CH_2Cl_2/hexanes 1/1) to afford the product (191 mg, 89%). The unstable product was used immediately in the next reaction.

^{1}H NMR (500 MHz, $CDCl_3$, 300 K, δ): 7.86 (t, J = 7.8, 1H), 7.71−7.68 (m, 2H), 7.57 (s, 1H), 7.51 (d, J = 7.9, 1H), 7.49 (d, J = 1.3, 1H), 7.43 (d, J = 7.8, 1H), 7.01 (d, J = 1.1, 1H), 7.00 (d, J = 8.0, 1H), 3.07 (t, J = 7.8, 2H), 2.65 (t, J = 7.7, 2H), 1.77−1.71 (m, 2H), 1.68−1.62 (m, 2H), 1.49−1.44 (m, 2H), 1.42−1.37 (m, 2H), 0.97−0.93 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, 300 K, δ): 155.4, 152.6, 152.3, 152.2, 144.3, 144., 143.1, 141.3, 140.7, 140.3, 137., 130.5, 126.2, 122.8, 119., 118.8, 118.7 (q, J_{C-F} = 320, 1C), 116.6, 114.9, 112.4, 32., 32.6, 30.3, 29., 22., 22.4, 14.1, 13.9. MS (ESI, m/z): 603.2 ($[M + Na]^+$).

*Compound **26c**.* This compound was prepared by the general Negishi cross-coupling procedure: component A, **26b** (0.081 mmol, 0.040 g); base, BuLi (0.090 mmol); $ZnCl_2$ (0.100 mmol, 0.015 g); catalyst, $Pd(PPh_3)_4$ (0.013 mmol, 0.015 g); component B, **26aTf** (0.12 mmol, 0.043 g). It was purified by column chromatography (silica,

CH_2Cl_2/hexanes 1/9, 1/4, 3/7, 2/3, 1/1) to afford a yellow waxy solid (11 mg, 20%).

^{1}H NMR (500 MHz, $CDCl_3$, 300 K, δ): 7.69 (dd, J = 15.9, 7.9, 2H), 7.56 (s, 1H), 7.55−7.43 (m, 6H), 7.42 (s, 1H), 7.22 (dd, J = 7.5, 0.6, 1H), 3.12 (t, J = 7.7, 4H), 2.65 (t, J = 7.6, 2H), 1.81−1.73 (m, 4H), 1.69 (s, 9H), 1.67−1.62 (m, 2H), 1.53−1.46 (m, 4H), 1.43−1.36 (m, 2H), 0.98−0.95 (m, 9H). ^{13}C NMR (125 MHz, $CDCl_3$, 300 K, δ): 163.2, 153.4, 153.4, 152.2, 151.9, 149.4, 144.7, 144.5, 144.1, 143., 143.22, 143.1, 138.7, 138.6, 138.1, 137., 137.01, 128.8, 127.8, 126.1, 122.6, 120.0, 119.8, 116.14, 116.11, 111.3, 110.4, 79.8, 32.9(2C), 32.7, 30., 29.9, 29.8, 28., 22.9(2C), 22.4, 14.14, 14.11, 13.9. HR-MS (ESI, $C_{43}H_{50}N_3OS_3$, $[M + H]^+$): calculated, 720.3110; found, 720.3118.

Compound ***26d***. This compound was prepared by the general Negishi cross-coupling procedure: component A, **26b** (0.21 mmol, 0.106 g); base, BuLi (0.22 mmol); $ZnCl_2$ (0.25 mmol, 0.034 g); catalyst, (SIPr)Pd(cin)Cl (0.010 mmol, 0.007 g);[21] component B, **26bTf** (0.19 mmol, 0.111 g). It was purified by column chromatography (deactivated alumina, CH_2Cl_2/hexanes 1/9, 1/4, 3/7, 2/3, 1/1) to afford a yellow waxy solid (44 mg, 25%).

^{1}H NMR (400 MHz, $CDCl_3$, 300 K, δ): 7.75−7.67 (m, 3H), 7.60−7.44 (m, 11H), 7.24 (d, J = 7.2, 1H), 7.02 (d, J = 0.8, 1H), 6.54 (d, J = 8.0, 1H), 3.21−3.13 (m, 6H), 2.67 (t, J = 7.6, 2H), 1.84−1.78 (m, 6H), 1.71 (s, 9H), 1.68−1.64 (m, 2H), 1.58−1.52 (m, 6H), 1.50−1.42 (m, 2H), 1.02−0.96 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, 300 K, δ): 163.2, 153.45, 153.42, 153.3, 152.2, 151.9, 151.8, 149.4, 144.7, 144.5, 144.1, 143.7, 143.6, 143.4, 143., 143.2, 138.8, 138.7, 138.6, 138.1, 137.1, 128.8, 128.7, 127.9, 126.1, 122.5, 120., 1120.0, 119., 116.3, 116.2, 111.3, 110.4, 79.8, 33.1, 33.0, 32.9, 32.7, 30.3, 30.0, 29.9, 28., 23.0, 22., 22.4, 14.2, 14.2, 14.1, 13.9. HR-MS (ESI, $C_{56}H_{63}N_4OS_4$, $[M + H]^+$): calculated, 935.3879; found, 935.3878.

Compound ***26TPT-H***. This compound was prepared by the general Negishi cross-coupling procedure: component A, 3-butylthiophene (7.10 mmol, 0.996 g); base, LiTMP (7.26 mmol); $ZnCl_2$ (10.10 mmol, 1.380 g); catalyst, in situ mixture of $Pd_2(dba)_3$ (0.20 mmol, 0.182 g), 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (IPr·HCl, 0.40 mmol, 0.170 g),[22] and potassium *tert*-butoxide (0.40 mmol, 0.045 g); component B, 2,6-dibromopyridine (3.38 mmol, 800 mg). It was purified by column chromatography (deactivated alumina, CH_2Cl_2/hexane 1/19, 1/12, 1/9) to give a pale yellow oil (0.745 g, 62% yield).

R_f(silica, AcOEt/hexane 1:9) = 0.69. ^{1}H NMR (400 MHz, $CDCl_3$, 300 K, δ): 7.63 (*t*, J = 8.36, 1H), 7.48 (d, J = 1.36, 2H), 7.43 (d, J = 7.80, 2H), 6.99 (d, J = 1.32, 2H), 2.64 (t, J = 7.62, 4H), 1.65 (J = 7.60, 4H), 1.39 (sextet, J = 7.40, 4H), 0.95 (t, J = 7.40, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, 300 K, δ): 152.2, 144.3, 144.1, 137.1, 126.1, 122.5, 116.4, 32.6, 30.3, 22.3, 13.9. HR-MS (ESI, m/z): $[M + H]^+$, $C_{21}H_{26}NS_2$, calculated 356.1501; found 356.1502; $[M + Na]^+$, $C_{21}H_{25}NNaS_2$, calculated 378.1320, found 378.1321.

Compound ***26TPT-CN***. This compound was prepared by the general Negishi cross-coupling procedure: component A, 3-butylthiophene (2.87 mmol, 402 mg); base, LiTMP (2.93 mmol); zinc chloride (3.45 mmol, 470 mg); catalyst, in situ mixture of $Pd_2(dba)_3$ (0.07 mmol, 56 mg), 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (IPr·HCl, 0.14 mmol, 60 mg),[22] and potassium *tert*-butoxide (0.14 mmol, 16 mg); component B, (2,6-dichloropyridin-4-yl)carbonitrile (1.15 mmol, 200 mg). It was purified by column chromatography (alumina, CH_2Cl_2/pentane 1/19, 1/9, 1/6) to give a yellow solid (200 mg, 45% yield).

R_f(silica, AcOEt/hexane 1/9) = 0.59. ^{1}H NMR (400 MHz, CDCl3, 300 K, δ): 7.57 (s, 2H), 7.51 (*d*, J = 1.40, 2H), 7.08 (d, J = 1.40, 2H), 2.65 (t, J = 7.64, 4H), 1.65 (quintet, J = 7.60, 4H), 1.39 (sextet, J = 7.40, 4H), 0.95 (t, J = 7.40, 6H). ^{13}C NMR (125 MHz, CDCl3, 300 K, δ): 153.4, 144.6, 142.2, 127.5, 124.4, 121.6, 117.2, 116.8, 32.6, 30.2, 22.3, 13.9. HR-MS (ESI, m/z): $[M + H]^+$, $C_{22}H_{25}N_2S_2$, calculated 381.1453, found, 381.1455; $[M + Na]^+$, $C_{22}H_{24}N_2NaS_2$, calculated 403.1273, found 403.1276.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures giving ^{1}H and ^{13}C NMR spectra and a CIF file, figure, and table giving X-ray crystallographic data for **26TPT-CN**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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■ REFERENCES

(1) Representative reviews: (a) Mishra, A.; Ma, C.-Q.; Bäuerle, P. *Chem. Rev.* **2009**, *109*, 1141−1276. (b) Perepichka, I. F.; Perepichka, D.; Meng, H.; Wudl, F. *Adv. Mater.* **2005**, *17*, 2281−2305. (c) Groenendaal, L.; Jonas, F.; Freitag, D.; Pielartzik, H.; R. Reynolds, J. R. *Adv. Mater.* **2000**, *12*, 481−494.

(2) Representative reviews: (a) Zhang, F.; Wu, D.; Xua, Y.; Feng, X. *J. Mater. Chem.* **2011**, *21*, 17590−17600. (b) Osaka, I.; McCullough, R. D. *Acc. Chem. Res.* **2008**, *41*, 1202−1214. (c) Murphy, A. R.; Fréchet, J. M. J. *Chem. Rev.* **2007**, *107*, 1066−1096.

(3) Representative reviews: (a) Meier, H. *Angew. Chem., Int. Ed.* **2005**, *44*, 2482−2506. (b) Mullekom, H. A. M.; Vekemans, J. A. J. M.; Havinga, E. E.; Meijer, E. W. *Mat. Sci. Eng.* **2001**, *32*, 1−40. (c) Roncali, J. *Chem. Rev.* **1997**, *97*, 173−206.

(4) We have found 2,6-biarylpyridines to be useful fluorophores in the context of chemosensor development. For representative examples, see: (a) Malashikhin, S.; Finney, N. S. *Org. Lett.* **2010**, *12*, 940−943. (b) Fang, A. G.; Mello, J. V.; Finney, N. S. *Tetrahedron* **2004**, *60*, 11075−11087.

(5) For polymers containing both pyridine and thiophene rings, see: (a) DuBois, C. J.; Reynolds, J. R. *Adv. Mater.* **2002**, *14*, 1844−1846. (b) Irvin, D. J.; DuBois, C. J., Jr.; Reynolds, J. R. *Synth. Met.* **2001**, *119*, 321−322. (c) Yamamoto, T.; Zhou, Z.; Kanbara, T.; Kizu, K.; Maruyama, T.; Nakamura, Y.; Lee, B.-L.; Ooba, N.; Tomaru, S.; Kurihara, T.; Kaino, T.; Kubota, K.; Sasaki, S. *J. Am. Chem. Soc.* **1996**, *118*, 10389−10399. (d) Jenkins, I. H.; Salzner, U.; Pickup, P. G. *Chem. Mater.* **1996**, *8*, 2444−2450.

(6) Pyridine−thiophene oligomers have attracted increased attention since the inception of this work. See: (a) Gholap, S. L.; Hommes, P.; Neuthe, K.; Reissig, H.-U. *Org. Lett.* **2013**, *15*, 318−321. (b) Wang, S.-A.; Hung, W.-Y.; Chen, Y.-H.; Wong, K.-T. *Org. Electr.* **2012**, *13*, 1576−1582. (c) Nanashima, Y.; Yokoyama, A.; Yokozawa, T. *J. Polym. Sci., Part A* **2012**, *50*, 1054−1061. (d) Bera, M. K.; Hommes, P.; Reissig, H.-U. *Chem. Eur. J.* **2011**, *17*, 11838−11843. (e) Liu, B.; Bao, B.; Du, D.; Wang, H.; Tian, J.; Bai, R. *Chem. Commun.* **2011**, *47*, 1731−1733. (f) Coluccini, C.; Manfredi, N.; Calderon, E. H.; Salamone, M. M.; Ruffo, R.; Roberto, D.; Lobello, M. G.; De Angelis, F.; Abbotto, A. *Eur. J. Org. Chem.* **2011**, 5587−5598. (g) De Giorgi, M.; Voisin-Chiret, A. S.; Santos, J. S. O. S.; Corbo, F.; Franchini, C.; Rault, S. *Tetrahedron* **2011**, *67*, 6145−6154. (h) Chevallier, F.; Charlot, M.; Katan, C.; Mongin, F.; Blanchard-Desce, M. *Chem. Commun.* **2009**, 692−694. (i) Yue, W.; Tian, H.; Hu, N.; Geng, Y.; Wang, F. *Cryst. Growth Des.* **2008**, *8*, 2352−2358. (j) Kumagai, A.; Fukumoto, H.; Yamamoto, T. *J. Phys. Chem. B* **2007**, *111*, 8020−8026. (k) Fukumoto, H.; Kumagai, A.; Fujiwara, Y.; Koinuma, H.; Yamamoto, T. 2006, *68*, 1349-1357.

(7) Rocha, S. V.; Finney, N. S. *Org. Lett.* **2010**, *12*, 2598−2601.

(8) For the preparation of 3-butylthiophene, see: McCullough, R. D.; Lowe, R. D.; Jayaraman, M.; Anderson, D. L. *J. Org. Chem.* **1993**, *58*, 904−912. For regioselective lithiation, see: Smith, K.; Barratt, M. L. *J. Org. Chem.* **2007**, *72*, 1031−1034.

(9) Negishi, E.; Zeng, X.; Tan, Z.; Qian, M.; Hu, Q.; Huang, Z. In *Metal-Catalyzed Cross-Coupling Reactions*, 2nd ed.; De Meijere, A., Diederich, F., Eds., Wiley-VCH: Weinheim, Germany, 2004; pp 815−889.

(10) For aryl methyl ether cleavage with Py·HCl, see: Loren, J. C.; Gantzel, P.; Linden, A.; Siegel, J. S. *Org. Biomol. Chem.* **2005**, *3*, 3105−3116.

(11) Fortman, G. C.; Nolan, S. P. *Chem. Soc. Rev.* **2011**, *40*, 5151−5169.

(12) 4-Cyano-2,6-dichloropyridine: Mello, J. V.; Finney, N. S. *Angew. Chem., Int. Ed.* **2001**, *40*, 1536−1538.

(13) The observation of facile electrochemical reduction alone is not sufficient to ensure *n*-type material character, and the determinants of *n*-type performance are not fully understood. See: (a) Chochos, C. L.; Tagmatarchisc, N.; Gregoriou, V. G. *RSC Adv.* **2013**, *3*, 7160−7181. (b) Anthony, J. E.; Facchetti, A.; Heeney, M.; Marder, S. R.; Zhan, X. *Adv. Mater.* **2010**, *22*, 3876−3892. (c) Newman, C. R.; Frisbie, C. D.; Bedras, J.-L.; Ewbank, P. C.; Mann, K. R. *Chem. Mater.* **2004**, *16*, 4436.

(14) For a discussion of Fc/Fc$^+$ as the reference standard of choice, see: (a) Cardona, C. M.; Li, W.; Keifer, A. E.; Stockdale, D.; Bazan, G. C. *Adv. Mater.* **2011**, *23*, 2367−2371. For the formal potential of Fc/Fc$^+$, see: Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877−910.

(15) Oligothiophenes capped on both ends by fluoroalkyl, fluorocarbonyl, or fluorobenzene groups are representative exceptions, serving as efficient *n*-type materials. For examples, see: Yoon, M.-H.; DiBenedetto, S. A.; Facchetti, A.; Marks, T. J. *J. Am. Chem. Soc.* **2005**, *127*, 1348−1349. (b) Yoon, M.-H.; DiBenedetto, S. A.; Russell, M. T.; Facchetti, A.; Marks, T. J. *Chem. Mater.* **2007**, *19*, 4864−4881. For a pyrimidine−thiophene conjugate that can undergo two-electron reduction, although it remains a *p*-type conductor, see: (c) Ortiz, R. P.; Casado, J.; Hernandez, V.; Navarrete, J. T. L.; Letizia, J. A.; Ratner, M. A.; Facchetti, A.; Marks, T. J. *Chem. Eur. J.* **2009**, *15*, 5023−5039.

(16) In general, for closely related species, the probabilities for spontaneous excitation and emission (and thus the extinction coefficient and quantum yield) are related. See: Calvert, J. G., Pitts, J. N., Jr. *Photochemistry*; Wiley: New York, 1966; pp 173−174.

(17) For recent examples of conducting *n*-type pyridinium polymers, see: (a) Izuhara, D.; Swager, T. M. *Macromolecules* **2011**, *44*, 2678−2684. (b) Izuhara, D.; Swager, T. M. *J. Am. Chem. Soc.* **2009**, *131*, 17724−17725.

(18) Lakowicz, J. R. *Principles of Fluorescent Spectroscopy*, 2nd ed.; Kluwer Academic: New York, 1999. (b) Demas, J. M.; Grosby, G. A. *J. Phys. Chem.* **1975**, *75*, 991−1024.

(19) Berlman, I. B. *Handbook of Fluorescent Spectra*; Academic Press: New York, 1965.

(20) Breit, B.; Seiche, W. *J. Am. Chem. Soc.* **2003**, *125*, 6608−6609.

(21) Marion, N.; Navarro, O.; Mei, J.; Stevens, E. D.; Scott, N. M.; Nolan, S. P. *J. Am. Chem. Soc.* **2006**, *128*, 4101−4111.

(22) Jafarpour, L.; Stevens, E. D.; Nolan, S. P. *J. Organomet. Chem.* **2000**, *606*, 49−54.